# Wolff–Kishner reduction type method for multi-walled carbon nanotubes

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Careful observation in the carbon cathode employed in the arc-discharge process for the synthesis of fullerenes by Iijima[1] led to the discovery of carbon nanotube (CNT), the name proposed for ultra thin carbon fibre with nanometre-size diameter and micrometre length. The originally obtained by-product in the synthesis of $C_{60}$ was only multi-walled carbon nanotubes (MWCNTs). 'CNTs are considered to be materials appropriate to realize intriguing characteristics related to the mesoscopic system based on their size and physico-chemical properties. In a macroscopic system in which both classical- and quantum-mechanical pictures become compatible, even for a short time if realized, its pragmatic significance would be very large considering technical level of today'[2]. It is, therefore, not surprising that many researchers have been attracted to this material and a large number of studies have piled up. The reported methods for the synthesis of CNTs include electric arc-discharge[3], laser vaporization[4,5], pyrolysis[6,7], chemical vapour deposition[8], etc. Catalysts like Fe/Co/Ni are used in some techniques. Is it possible to dispense with these catalysts so that the as-prepared sample will be of high purity?

In their search for a cost-effective method to produce MWCNTs, Wang *et al.*[9] adopted a modified Wolff–Kishner reduction process employing ethyl alcohol as a source of carbon and also solvent in the absence of Fe/Co/Ni. MWCNTs obtained by the reduction of ethyl alcohol with a high concentration of sodium borohydride ($NaBH_4$) in a strong basic solution without the addition of the conventional catalysts like Fe/Co/Ni are of high purity.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of the as-prepared sample (Figure 1 *a*, *c*) reveal a straight morphology. The synthesized MWCNTs have an outer diameter in the range of 10–40 nm and a length of up to 25 μm. The inner diameters are 3–6 nm. That some nanotubes possess bamboo-like structures have also been indicated (Figure 1 *b*, *d*). Images of the tip show that all nanotubes have closed ends with different shapes. For instance, one can see that some CNTs have a conical-tip structure (Figure 1 *c*).

HRTEM of an individual MWCNT shows that the inner wall spacing is about 0.34 nm (Figure 2 *a*), in accordance with the standard spacing. Selected area electron diffraction pattern has also established that the nanotube is well-crystallized. The as-prepared sample also contains some MWCNTs with small inner diameters (~2 nm) and with outer diameter of ~20 nm (Figure 2 *b*).

The protocol for the synthesis is simple. In a typical experiment, a mixture of 80 ml of ethyl alcohol (90%), 4.2 g $NaBH_4$ (99.99%) and 15 ml of 10M NaOH solution was stirred for about 30 min and then transferred to a Parr reactor (capacity 125 ml) and sealed. It was kept at 180°C for 20 h and then cooled to room temperature. The products were washed several times with alcohol and distilled water and then dried in a vacuum oven at 60°C for 10 h. The authors envisage that ethyl alcohol reacts with $NaBH_4$ in high concentration and strong basic condition to yield $H_2$, triethyl borate $(OC_2H_5)_3B$ and other alkoxy borohydrides. $(OC_2H_5)_3B$ decomposes to $B_2O_3$ and oxygen containing hydrocarbon, which further disintegrates to form nanotubes and other chemicals. It is observed that CNTs are formed only in the presence of high concentration of NaOH. From SEM and TEM studies, it is shown that the yield of as-prepared CNTs is ~50%. It may be mentioned here that Wolff–Kishner reduction was discovered independently in Germany[10] and Russia[11]. In the classical method, a ketone (or aldehyde) is converted to the corresponding alkane and nitrogen by converting the carbonyl compound into a hydrazone by heating in a sealed tube or an autoclave with the base sodium ethoxide in absolute ethanol (eq. 1).

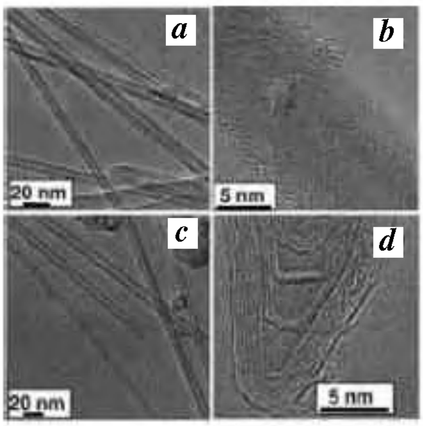

Figure 1. *a*, *b*, TEM and HRTEM images of the as-prepared carbon nanotubes. *c*, *d*, Carbon nanotubes with bamboo-like structure. Carbon nanotubes with conical-tip structure (reproduced from ref. 9 with permission from W. Wang).

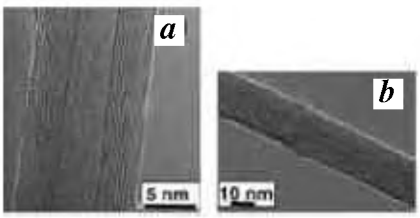

Figure 2. (*a*) HRTEM image and (*b*) high-magnification TEM image of an individual CNT showing small inner diameter of about 2 nm (reproduced from ref. 9 with permission from W. Wang).

$$>C{=}O \xrightarrow{H_2NNH_2} >C{=}NNH_2 \xrightarrow[200^{\circ}C]{NaOC_2H_5} >CH_2 + N_2 \quad (1)$$

The merits of the modified Wolff–Kishner reduction method applied in the synthesis of MWCNTs are: (i) ethyl alcohol acts as a source of carbon and also as the solvent, providing a route for low cost production and performing the reaction under mild conditions, and (ii) as-prepared CNTs are highly pure as no catalysts like Fe/Co/Ni are introduced during synthesis. Thus a new route is now available for the synthesis of CNTs.

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**COMMENTARY**

# Infirmities and inconsistencies of Indian legislations on access and benefit sharing

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India, occupying 2.45% of the world's land area, has 16.8% of the world's population and shares a meagre 1.6% of the world's GDP[1]. With equally skewed internal distribution of this domestic product, the country has the highest incidence of poverty and malnutrition. Nearly 30% of the world's poor, who are living on less than I US $ a day, are Indians. In contrast, India has a rich biodiversity with more than 15,000 endemic plant species[2] and a major share of two of the 12 megabiodiversity centres of the world. India is the primary and secondary centre of diversity for about 168 crop and fruit tree species, with equally rich genetic diversity in few other crops. More than 60% of Indians, a good proportion of them poor, are dependent on agriculture and related activities, which contribute one-fourth of the GDP. There is perhaps no other region in the world, where such a huge population is so much dependent on biodiversity for livelihood, food and health security. This way of life of people over centuries had contributed a rich genetic diversity and traditional knowledge on its use and conservation. Therefore, national legislations seeking to safeguard the national wealth against piracy and to conserve and promote the way of living, livelihood, food and health security of vast majority of Indians have immense public interest.

Access and benefit sharing (ABS) is an important principle of equity recognized and legitimized by the Convention on Biological Diversity (CBD). 'Fair and equitable sharing of the benefits arising out of the utilization of genetic resources, including by appropriate access to genetic resources and by appropriate transfer of relevant technologies, taking into account all rights over these resources and to technologies, and by appropriate funding' is set out as one of the three overriding objectives of the CBD[4]. Benefit sharing is a legitimate reward to the community *albeit* the country for generating genetic diversity and associated traditional knowledge, conserving them with sustainable use and making them available. The CBD paradigm recognizes the sovereign rights of countries over their biological resources and associated knowledge[5], and the need for facilitated access to these resources and knowledge by others. The Member countries, which are Parties to the CBD, are required to enact and enforce their own national laws in consistence with the CBD to assert the said sovereign rights and to establish an ABS system[6].

Two recent Indian legislations, which deal with ABS system are the Protection of Plant Varieties and Farmers' Rights Act (PPVFR Act), 2001 and the Biological Diversity Act (BD Act), 2002. The PPVFR Act was enacted to make India TRIPS compliant with respect to grant of intellectual property protection on plant varieties[7]. The BD Act seeks to establish national sovereignty over the bio-resources and associated traditional knowledge existing within legal territorial bounds, including the economic zone in sea, in pursuance of the CBD and to provide regulation for its conservation, sustainable use and access of its components and ensuring fair and equitable sharing of benefits arising out of its use[8]. This note examines the ABS mechanism provided in these two Acts and discusses the inconsistencies and infirmities therein.

## The Biological Diversity Act

The route of access to Indian biological resources and associated knowledge provided in the BD Act differs depending on whether the party accessing is (1) a non-Indian or non-resident Indian citizen, or a body corporate/association/organization not incorporated or registered in India or such bodies having non-Indian participation in capital or management; (2) Indian citizen or a body corporate/association/organization registered in India, and (3) local people and communities inhabiting an area, including traditional medicine practitioners. Access by parties belonging to the first group has to be necessarily with prior approval of the National Biodiversity Authority (NBA)[9]. This access is facilitated through a structured application and payment of Rs.10,000 (US$ 230) as fee. This application largely conforms to the Bonn Guidelines[10]. An access request is expected to be decided within six months time. BD Act has no explicit provision to involve the concerned local community in the decision making with prior informed consent on traditional knowledge associated with the use of genetic resources. The Act, however, provides for the involvement of Biodiversity Management Committee, which is instituted at each Panchayat, in the process of decision making on ABS issues related to local